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**WPI Accession Number 87-219590/31 (CELLULOSE), &**  
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**(HIGH MOLECULAR), & SU 325234**

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(54) **Improvements in or relating to organic compounds**

(57) A polymeric product which is the reaction product of  
a) chitosan (herein defined as component A) with  
b) a methoxyphenyl-containing aldehyde, ketone or acid (preferably in solution form) preferably derived from a natural product; the natural product preferably having a molecular weight of at least 10,000 and preferably being derived from lignin (herein defined as component B), e.g. veratraldehyde, salicylaldehyde, vanillin, syringaldehyde, etc. The product is film-forming and can be used in packaging.

**GB 2 272 447 A**

## IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

Polysaccharides can be classed into different solubility groups, according to structure and conformation, based on experimental findings. Linear polysaccharides, such as cellulose and chitin, form highly-ordered crystalline arrays which are difficult to dissolve due to cohesive forces. Highly-branched polysaccharides are soluble as a rule, starch being an example. Solubility may be affected by ionic groups present in the polysaccharide, low molecular weights and other parameters, but no prediction can be made as to the behavior of novel modified polysaccharides; these should be determined experimentally.

Chitosan is a polysaccharide which has not been extensively used and which possesses many of the desired characteristics for a packaging material. It is already known to be suitable for biomedical and technological applications, due to its special properties, i.e. cationicity and filmogenicity. The primary amino group of chitosan, which lends itself to soluble salt formation with a restricted number of weak acids, has been derivatized in various ways in order to impart novel properties to chitosans. Early works in this field include those with anhydrides (S. Hirano et al, Carb. Res. (1976) 47, 315), simple aldehydes (S. Hirano et al, Carb. Res. (1979) 71, 344), aldehydoacids, such as glyoxylic acid (R. Muzzarelli et al, Carb. Res. (1982) 107, 199), ketoacids (R. Muzzarelli, US Patent 4,835,265 (1986)), and a number of other reagents among which monochloroacetic acid, aldoses, ketoses (L.D. Hall and M. Yalpani, US Patent 4,424,346 (1984)) and salicylaldehyde (G.A.F. Roberts, in "Chitin in Nature and Technology", R. Muzzarelli et al, eds., Plenum Press, New York (1986)). Similarly, effective metal ion sequestering agents in which are included various chitosan amide derivatives wherein the carboxylic substituents, including amino acids, have been introduced, have been disclosed (J. Vanlenberghe et al, US Patent 3,879,376 (1975)). Modified chitosans have also been cross-linked to prevent dissolution (Koshugi, US Patent 4,373,096 (1983)). Starch has been oxidized and submitted to reductive amination in order to prepare deoxyaminated polysaccharides (M. Yalpani, US Patent 4,683,298 (1987)). Hydrophobe-modified cationic polysaccharides ionically combined with

hyaluronic acid have also been disclosed (G.L. Brode et al, US Patent 4,767,463 (1988)). All of these works are expressly directed to the enhancement of the chelating ability of chitosan towards metal ions.

As a matter of fact, polyelectrolyte complex formation is another field in which, for various purposes, different polysaccharides have been combined with each other, in general to produce capsules or beads capable of including fragrances or drugs. Examples are the works on chitosan and alginate (M.M. Daly and D. Knorr, *Biotechnol. Progr.* (1988) 4, 76), on chitin and alginate (Y. Takahashi, *J. Inclusion Phen.* (1987) 5, 525), on chitosan and O-carboxy-methyl cellulose (W. Arguelles et al, *Makromol. Chemie* (1988) 9, 693), on chitosan and hyaluronic acid (K. Takayama et al, *Chem. Pharm. Bull.* (1990) 38, 1993), on chitosan and polyacrylic acid (T. Takahashi et al, *Intl. J. Pharmaceutics* (1990) 61, 35), on chitosan and starch (T. Kume and M. Takehisa, *Rad. Phys. Chem.* (1984) 23, 579; K. Shimoda et al, *Jpn. Kokai Tokyo Koho* (1979) 79-73, 463), on chitosan and oxidized cellulose (J. Hosokawa et al, *Ind. Eng. Chem. Res.* (1990) 29, 800) and on chitosan and carboxymethyl starch (T. Nakajima and I. Asako, *Jpn. Kokai Tokyo Koho* (1989) 01,156341). In these cited works, emphasis is on the polyelectrolyte complex formation.

Chitosan has filmogenic ability and chitosan films have been manufactured for a long time by casting a chitosan salt solution on a glass plate and drying (for a review, R. Muzzarelli, *Chitin*, Pergamon Press, Oxford (1977)). Such films, once neutralized, are no longer soluble in pure water where they swell in any case, but easily dissolve in weak acid solutions. As a consequence, chitosan films have found few applications. The same can be said for chitin/chitosan filaments, despite efforts to upgrade such products (see for instance K. Motosugi et al, *Eur. Patent Application* 0,171,254 (1985)). The few modified chitosans having filmogenic ability have been difficult to exploit commercially because they are too expensive to produce and due to unfavorable price/performance ratios. This is unfortunate because chitosan-based films, being of natural origin, could possibly solve a number of problems. For instance, in the field of packaging technology, a wide variety of synthetic polymers are used. However, much of that material has a short life span and generally ends up in rubbish disposal within one or two years. Lack of degradation of those polymers is posing a consider-

able problem and recently there has been a drive to find polymers that are biodegradable.

To this end, according to the invention there is provided a polymeric product which is the reaction product of

- a) chitosan (herein defined as component A) with
- b) a methoxyphenyl-containing aldehyde, ketone or acid (preferably in solution form) preferably derived from a natural product; the natural product preferably having a molecular weight of at least 10,000 and preferably being derived from lignin (herein defined as component B).

Preferably the reaction occurs at a pH of less than 7; preferably the reactants are in solution, dispersion or suspension.

We have found that the degree of substitution obtained ranged from about 30-75% for the chitosans.

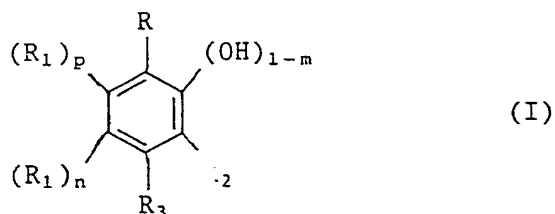
Preferably the molecular weight of the chitosans of Component A are from 100,000-1,000,000 more preferably 200,000 to 600,000.

Further according to the invention, there is provided a crystalline or partially-crystalline modified chitosan, in aldimine and secondary amine form, preferably resulting from reacting chitosan powder with a methoxyphenyl-containing aldehyde.

We have found that a chitosan powder (preferably amorphous), reacted under heterogeneous or homogenous conditions with a specific group of aromatic aldehydes, yields crystalline or partially-crystalline modified chitosans in both aldimine and hydrogenated (secondary amine) forms. (This means that those aldehydes are capable of imparting a novel structural order to amorphous chitosan subsequent to reaction and to favor association of polymer chains by cohesive forces, leading to novel unpredicted physico-chemical characteristics.)

Preferably components A and/or B are in solution, dispersion or suspension. More preferably components A and B are either both in organic or both in aqueous form, most preferably aqueous solutions.

Preferably component B is a compound of formula I



in which R is -CHO, -COOH or -COCH<sub>3</sub>;

R<sub>1</sub> is hydrogen, C<sub>1-6</sub>alkyl or C<sub>1-6</sub>alkoxy;

R<sub>2</sub> is hydrogen, C<sub>1-6</sub>alkyl or C<sub>1-6</sub>alkoxy;

R<sub>3</sub> is OH, C<sub>1-6</sub>alkoxy or a residue of lignin bound to the phenyl group through an ether group or hydrogen;

m = 0 or 1 (independently of n or p);

n = 0 or 1 (independently of m or p); and

p = 0 or 1 (independently of m or n).

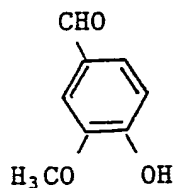
Preferably one of n and p is 0 and the other of n and p is 1.

Preferably R<sub>1</sub> is R<sub>1</sub>' where R<sub>1</sub>' is hydrogen, C<sub>1-4</sub>alkyl or C<sub>1-4</sub>alkoxy, more preferably R<sub>1</sub>" where R<sub>1</sub>" is hydrogen, methyl or methoxy.

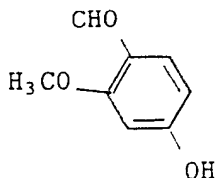
Preferably R<sub>2</sub> is R<sub>2</sub>' where R<sub>2</sub>' is hydrogen, C<sub>1-4</sub>alkyl or C<sub>1-4</sub>alkoxy, more preferably R<sub>2</sub>" where R<sub>2</sub>" is hydrogen, methyl or methoxy.

Preferred aldehyde compounds of formula I are veratraldehyde (3,4 dimethoxybenzaldehyde), salicylaldehyde (2-hydroxybenzaldehyde),

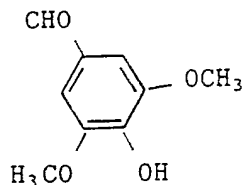
vanillin, a compound of the formula



o-vanillin, a compound of the formula

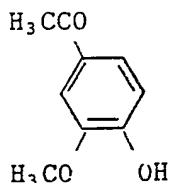


syringaldehyde, a compound of the formula



guaicol, acetosyringaldehyde and p-hydroxybenzaldehyde.

A preferred ketone of formula I is acetovanillone, a compound of the formula



Preferred acids of formula I are p-hydroxybenzoic acid, vanillic acid, proto catechuic acid, syringic acid and ferulic acid.

Preferred acids for dissolving the chitin and chitosan are selected from formic acid, malic acid, acetic acid and lactic acid.

The preferred aldehydes are those industrially obtained from the chemical degradation of lignin, whose functionality mainly includes the syringyl and guaiacyl groups corresponding to 3,5-dimethoxy-4-hydroxyphenyl and to 4-hydroxy-3-methoxyphenyl groups, respectively. Vanillin, syringaldehyde and veratraldehyde are major products from hardwood lignins. O-Vanillin is also very suitable for use in the present invention.

All of these aldehydes are distinguished by the fact that they carry desirable methoxyphenyl groups. They react with chitosan within a matter

of minutes. In fact, the most straightforward way to introduce the desired methoxyphenyl functions into chitosan is by the reaction of chitosan with methoxyphenyl aldehydes via Schiff base formation at room temperature and subsequent or concomitant optional reduction. Salicylaldehyde and 2-hydroxybenzaldehyde may similarly be used.

The aldehydes used in the invention are soluble in ethanol and in ether. Two of them (vanillin and syringaldehyde) are also soluble in acetic acid and veratraldehyde is soluble in glacial acetic acid. Acetic acid is also the preferred solvent for chitosan; reactions could therefore be carried out in homogeneous (acetic) solutions. The Schiff reaction, therefore, appears to be feasible under both heterogeneous and homogeneous conditions.

After evaporation of the solvent, all of the aldimines obtained under homogeneous conditions were surprisingly found to be insoluble in aqueous media and in alcohol. Those from syringaldehyde and vanillin were soluble in acetic acid but the other ones were not.

The aldimines treated with a dilute solution of hydrogenating products preferably sodium borohydride, and thus hydrogenated to secondary amines, once dried, were surprisingly found to be insoluble in all aqueous media tested, including hydrochloric acid, sulfuric acid and sodium hydroxide dilute solutions.

With the present invention, the typical functional groups of lignin, namely the guaiacyl, veratryl and syringyl moieties, as well as similar ones, are introduced into chitosan via Schiff reaction and optional hydrogenation. High degrees of substitution can be achieved. As a consequence, chitosan lends itself to the preparation of lightly colored insoluble materials. Acetic acid solutions of the guaiacyl, veratryl and syringyl chitosans are useful for film casting.

All of these modified chitosans possess a certain degree of crystallinity. In particular, o-vanillin, the methoxyphenyl aldehyde which is collected to the greatest extent on chitosan, introduces the biggest number of apparent changes in the FTIR and x-ray diffraction spectra and

leads to fairly insoluble materials, hydrogenated or not; the aldimine itself is a bright yellow, insoluble and crystalline product.

Methoxyphenyl aldehydes are therefore surprisingly found to be the only class of aromatic aldehydes which lead to insoluble or sparingly-soluble modified chitosans, in contrast to unsubstituted aliphatic and aromatic aldehydes, which yield enormously swollen gels, such as those obtained from n-alkyl aldehydes and benzaldehyde (as discussed in R. Muzzarelli et al, J. Membrane Sci. (1983) 16, 295) and at variance with carboxylated aliphatic and aromatic aldehydes such as glyoxylic acid and o- and p-phthalaldehydes which yield as a rule water-soluble modified chitosans, due to their amphoteric nature (as discussed in R. Muzzarelli et al, Carbohydr. Pol (1982) 2, 145).

It was further observed that aldimine chitosans and hydrogenated aldimine chitosan solutions of the present invention in both crude or dialyzed forms were not only suitable for film casting but also gave films of exceptional characteristic properties, compared to plain chitosan films.

They are, unexpectedly, found to yield films of enhanced strength, mainly due to novel polymeric chain arrangements favored by the methoxyphenyl functions. The novel characteristics for the veratraldehyde modified chitosan are: general insolubility, moderate water repellency, high mechanical resistance, biodegradability, attractive brilliant silver tone, absence of shrinking, possibility of ironing and thermal shaping, innocuity and safety.

Further there is provided according to the invention a polymeric composition resulting from adding

- a) a naturally occurring cationic polymer [hereinafter defined as component i)] (preferably chitin and/or chitosan or derivatives thereof, including component A; preferably high molecular weight, more preferably 100,000 to 1,000,000 most preferably 200,000 to 600,000) to
- b) a non-ionic polysaccharide and/or a lignin (e.g. Kraft lignin) or lignosulphonate [herein defined as component ii)].



Preferably the cationic polymer of component i) is in solution, dispersion or suspension.

Preferably component ii) is also in the form of a solution, dispersion or suspension.

Preferred polysaccharides of component i) are selected from dextran, modified celluloses and sorbitol, more preferably starch.

The polymeric composition is preferably prepared by dissolving the cationic polymer (preferably chitin or chitosan) in an acidic aqueous medium and adding this to an aqueous polysaccharide (preferably starch) solution or an aqueous dispersion of Kraft lignin or lignosulphonates with vigorous mixing preferably at 20-60°C for preferably 2-12 hours to form a relatively high viscous gel.

Preferably the ratio of component i) to ii) is 10:90 to 70:30, more preferably 30:70 to 70:30, most preferably about 50:50.

Preferably the degree of acetylation of the chitosans is 0 to 45%, more preferably 15 to 30%, most preferably 17 to 25%.

The polymeric products and/or polymeric compositions according to the invention are biodegradable to at least 50% over 60 days according to the STURM test or the modified STURM Test or with respect to ASTM G21.

Preferably the biodegradability is at least 60%, more preferably at least 70%, most preferably at least 90%, especially at least 95-100% over 60 days according to the modified STURM test.

We have found that lignin itself can be dispersed in a chitosan solution. Within seconds, the viscosity of these dispersions increased dramatically and led to a paste. By drying the paste, shaped bodies could be obtained having exceptional mechanical and tensile characteristics and insolubility. In spite of the fact that both chitosan and lignin separately were scarcely crystalline, x-ray analysis revealed that a certain degree of crystallinity was achieved upon mixing and drying. Through a scanning electron microscope, regularly ordered

regions in the form of bunches of rods could be observed. Notwithstanding air bubbles and undissolved chitin particles (which could be avoided by filtering the solution under vacuum), hardness was found to be similar to plywood.

Analogous results were obtained by introducing corn starch into a chitosan solution. The chitosan and starch combination, once dried, was as unbreakable as plywood and tools were needed to cut it, even when thickness was just 3 mm. The acids used to dissolve the chitosan powder, namely malic, formic, acetic and lactic acids were practically equivalent.

Where Kraft lignin or lignosulphonate is used, this invention can help to avoid waste of these products.

Thus the present invention has alleviated some difficulties inherent in making films, filaments and shaped objects with modified chitosans, by providing a novel class of modified chitosans, particularly suited for this purpose. Moreover, it has met expectations related to biodegradability of films of technical importance, particularly in the packaging field.

Polymers according to the invention have very low toxicity.

Polymers according to the invention can be used for packaging material, especially for food and pharmaceutical products (e.g. blister packs for pharmaceuticals) due to their low toxicity; for encapsulation (slow release) of agro chemicals; for any throw-away articles (such as bottles and packs); for sheets used in plant growth for covering soil, leaving the plant exposed (e.g. for strawberry growing); and for sheets covering plants totally.

The invention will now be illustrated by the following Examples.

Example 1

Reactions under heterogeneous conditions

Trials are carried out with each aldehyde (0.10 g) dissolved in ethanol (3 ml). Those solutions are further diluted for analytical purposes up to 75 ml with a water-ethanol mixture containing 3% ethanol.

Characteristic absorption bands for the 4 phenolic aldehydes in the range 200-400 nm are the following:

o-vanillin, 217 (max), 263, 340 nm  
vanillin, 203, 229 (max), 278, 308  
syringaldehyde, 213 (max), 305 nm  
dihydroxybenzaldehyde, 205 (max), 229, 278, 309

The water-ethanol solution (3%) is used for tracing reference curves and for determining the collection of aldehydes by chitosan powder (Protan 027-572-02; 180-350 micron). The quantities in reciprocal presence are in all cases 150 mg chitosan and 150 mg aldehyde.

Results, shown in Table I, indicate that o-vanillin is particularly reactive towards chitosan, because it is collected to a remarkable extent (35%) within the first 30 min of contact. At equilibrium (3 days), more than one half is collected (54%), which means that one weight of chitosan reacts with more than one half that weight of o-vanillin. Syringaldehyde and vanillin in the order react to a remarkable extent; 3,4-dihydroxybenzaldehyde give the lowest percentage. For the aldimine obtained from o-vanillin, it is estimated that about one half of the available amino groups in chitosan undergo Schiff reaction.

Table I

Collection percent of aldehydes by chitosan powder (150 mg, 180-350 micron) at 25°C, pH 5.0, from water-ethanol (3%) solutions.

Aldehyde	10 min	30 min	1 hour	4 hours	3 days
o-vanillin	23	35	-	45	54
vanillin	-	25	-	30	38
syringaldehyde	7	17	25	-	43
3,4-dihydroxybenzaldehyde	7	13	-	-	20

#### Crystallinity of the products

The x-ray diffraction spectra obtained on the powders prepared as indicated above show the presence of diffraction peaks in all samples for the aldimines and their reduction products. The data are shown in Table II.

The chitosan used (Protan 027-572-02) is remarkably free of any degree of crystallinity. In general, chitosans exhibit two main diffraction peaks centered around 9 and 19 2-theta values, indicative of their structural and conformational features (020 and 110 reflections, respectively). They are known to be strongly reduced by harsh chemical treatments and the 020 crystallographic plan can be totally destroyed by mechanical treatments.

In the present case, aldimine formation leads to crystalline products having one reflection at 19.76-20.08 2-theta values.

For o-vanillin, preparations are made under homogeneous conditions and enhanced crystallinity is observed also in the case of the reduced aldimine (4.22, 14.22 and 20.22 2-theta).

The hydrogenation of the aldimine double bond leads to crystallinity increase in the case of o-vanillin and syringaldehyde for which novel

reflections are detected at 5.62 and 8.08 2-theta values, respectively (Table II).

Table II

X-Ray diffraction data (2-theta values) for the chitosan derivatives obtained from aldehydes by Schiff reaction.

Aldehyde	Aldimine		Hydrogenated product	
HETEROGENEOUS CONDITIONS				
o-vanillin	20.08	f	5.62	s 20.07 f
vanillin	19.76	s		19.66 s
syringaldehyde	19.84	s	8.08	f 20.00 b
3,4-dihydroxybenzaldehyde	19.86	m		20.02 b
HOMOGENEOUS CONDITIONS				
o-vanillin	4.22	s 20.22 m	4.94	s 20.30 m
-----				
f=faint; m=medium; s=strong; b=broad				

#### Chemical identity of products

The chemical identity of the modified chitosan is proved by FT infrared spectrometry, which also provides evidence of the modification.

o-vanillin + chitosan: Novel bands not found in chitosan and corresponding to spectral features of o-vanillin are in the region 700-800 and at  $1480\text{ cm}^{-1}$ , while the  $1550\text{ cm}^{-1}$  band is no longer evident and the one at  $1650\text{ cm}^{-1}$  is strengthened. On the basis of the second derivative FTIR spectra, the main differences between the aldimine and the reduced product are at  $1530\text{ cm}^{-1}$  as expected for a secondary amine formation, while shiftings occur at 1470-1500 and  $1250\text{--}1270\text{ cm}^{-1}$ .

vanillin + chitosan: There is no impressive difference between the aldimine and reduced product; novel bands are at 1500, 1450, 1260 and 800 with strengthening of the  $1550\text{ cm}^{-1}$  band.

syringaldehyde + chitosan: No remarkable difference is found between the aldimine and the reduction product spectra. Novel bands are at 1500, 1450, 1220 and 820  $\text{cm}^{-1}$ .

dihydroxybenzaldehyde + chitosan: Some difference is visible at 1500 and novel bands are at 1250 and 820  $\text{cm}^{-1}$ .

In all cases, novel bands are found in the spectra of chitosan reacted with the phenolic aldehydes. The novel bands correspond to typical bands assigned to the phenolic moieties chemically introduced into chitosan.

#### **Absence of chelating ability**

The above materials are contacted with aqueous metal ion solutions (cobalt, chromium-III, nickel and copper) at pH 5-6 and found not to collect said metal ions to any appreciable extent by atomic absorption spectrometry.

#### Example 2

##### **Film casting from crude non-hydrogenated solutions**

Chitosan powder is dissolved in 1% acetic acid. Veratraldehyde is dissolved in glacial acetic acid.

The weight ratio 1:2 veratraldehyde/chitosan is preferred. A higher than usual chitosan concentration (1.7%) is also chosen to have shorter evaporation times. Evaporation of these solutions (50 or 100 g) is done in polystyrene Petri dishes (12x12 cm) at 25°C (3 days) and at 50°C (overnight). The latter conditions are found to be preferable because the upper film surface results flat and smooth, which is not the case for films dried at room temperature whose upper surface exhibits unusual waves. Films are allowed to equilibrate with room humidity before removal from the dishes. Once removed from the dishes, the films are dipped into a hydrogenating bath containing sodium borohydride (1.0 g), water (450 ml) and ethanol, hospital grade (250 ml). The latter is added just to slow down the hydrogen release. Films are kept submerged into this bath for 10 min with occasional stirring.

After drying at 25°C between filter paper sheets, the films show an attractive silver tone with one face more brilliant (dish contact face) than the other, high resistance to traction and perforation and possibility of ironing at moderate temperature.

The films are insoluble in water, with some degree of hydrorepellency, insoluble in dilute acetic, sulfuric and hydrochloric acids, insoluble in dilute sodium hydroxide as well as in common solvents.

### Example 3

#### Film casting from hydrogenated and dialyzed solutions

A crude solution of chitosan aldimine is hydrogenated after pH adjustment (4.2) and dialyzed against water for 3 days in a dialysis tube (cutoff 15,000). Films cast from this solution are insoluble but the freeze-dried material was soluble. The films obtained are much more transparent than those described in the previous section.

#### Susceptibility to enzymatic degradation

By measuring the viscosity of a 1.4% solution prepared by dissolving the freeze-dried material above, it is verified that the modified chitosan is biodegradable. In the presence of 10 mg of lysozyme at pH 4.7 the viscosity is reduced to about 10% of the initial value within 50 min.

### Example 4

#### Products made of chitosan malate and starch

Chitosan (32 g) is suspended in water (130 ml) and after soaking, is dissolved by adding malic acid (6 g in 30 ml). Then maize starch (32 g) is added under vigorous stirring. After a couple of minutes, a thick paste is obtained, which is spread on an aluminum perforated dish and dried overnight in a ventilated oven at 50°C. The resulting product in the form of 3 mm thick bar is as rigid as plywood (instrumentally measured) and insoluble in water or slightly acidic solutions, even after two-week soaking.

Example 5

Products made of chitosan lactate and lignin

Chitosan (30 g) is suspended in water (160 ml) and after soaking, is dissolved by adding lactic acid (6 ml, 90% solution). Kraft lignin (30 g) is then added under vigorous stirring (pH rose from 5.8 to 7.6). The resulting paste is treated as in Example 8 and the final product (3 mm thick) is as hard as plywood and insoluble.

Example 6

Products made of chitosan acetate and starch

14 g of a commercially available chitosan (FLONAC - ultra fine) is mixed very thoroughly in 200 mls of water and 2 mols of glacial acetic acid. This is vigorously stirred for 30 minutes to produce a practically clear gel.

14 g of starch (from corn) is dissolved in 100 mls of water and then the chitosan mass is slowly added under steady stirring. A lightly opaque gel results.

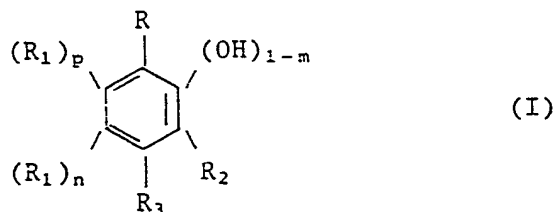
The mass is then dried for 60 minutes at 160°C by contact with two heated plates.

Freeze-drying, microwave treatment and ironing are also found to be suitable drying means.



CLAIMS

1. A polymeric product which is the reaction product of
  - a) chitosan (herein defined as component A) with
  - b) a methoxyphenyl-containing aldehyde, ketone or acid (preferably in solution form) preferably derived from a natural product; the natural product preferably having a molecular weight of at least 10,000 and preferably being derived from lignin (herein defined as component B).
2. A product according to Claim 1 in which component A) is a crystalline or partially-crystalline modified chitosan, in aldimine and secondary amine form.
3. A product according to Claim 1 or Claim 2 in which components A and/or B are in solution, dispersion or suspension.
4. A product according to any one of the preceding claims in which component B is a compound of formula I



in which R is -CHO, -COOH or -COCH<sub>3</sub>;

R<sub>1</sub> is hydrogen, C<sub>1-6</sub>alkyl or C<sub>1-6</sub>alkoxy;

R<sub>2</sub> is hydrogen, C<sub>1-6</sub>alkyl or C<sub>1-6</sub>alkoxy;

R<sub>3</sub> is OH, C<sub>1-6</sub>alkoxy or a residue of lignin bound to the phenyl group through an ether group or hydrogen;

m = 0 or 1 (independently of n or p);

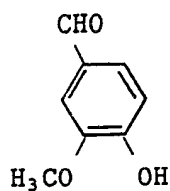
n = 0 or 1 (independently of m or p); and

p = 0 or 1 (independently of m or n).

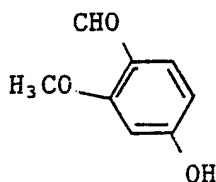
5. A product according to Claim 4 in which R<sub>1</sub> is R<sub>1</sub>' where R<sub>1</sub>' is hydrogen, C<sub>1-4</sub>alkyl or C<sub>1-4</sub>alkoxy.

6. A product according to Claim 5 in which  $R_1$  is  $R_1''$  where  $R_1''$  is hydrogen, methyl or methoxy.
7. A product according to any one of Claims 4 to 6 in which  $R_2$  is  $R_2'$  where  $R_2'$  is hydrogen,  $C_{1-4}$ alkyl or  $C_{1-4}$ alkoxy.
8. A product according to Claim 7 in which  $R_2$  is  $R_2''$  where  $R_2''$  is hydrogen, methyl or methoxy.
9. A product according to any one of the preceding claims in which component B is veratraldehyde (3,4 dimethoxybenzaldehyde), salicylaldehyde (2-hydroxybenzaldehyde),

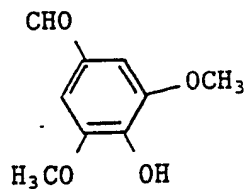
vanillin, a compound of the formula



o-vanillin, a compound of the formula

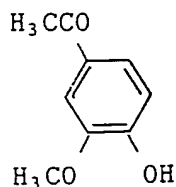


syringaldehyde, a compound of the formula



guaicol, acetosyringaldehyde and p-hydroxybenzaldehyde; or

acetovanillone, a compound of the formula



or p-hydroxybenzoic acid, vanillic acid, proto catechuic acid, syringic acid and ferulic acid.

10. A polymeric composition resulting from adding
  - a) a naturally occurring cationic polymer [hereinafter defined as component i)] to
  - b) a non-ionic polysaccharide and/or a lignin or liginosulphonate [herein defined as component ii)].
11. A composition according to Claim 10 in which the cationic polymer of component i) is in solution, dispersion or suspension.
12. A composition according to Claim 10 or Claim 11 in which component ii) is also in the form of a solution, dispersion or suspension.
13. A composition according to any one of Claims 10 to 12 in which the polysaccharides of component i) are selected from dextran, modified celluloses and sorbitol and starch.
14. A composition according to any one of Claims 10 to 13 in which the ratio of component i) to ii) is 10:90 to 70:30.

**Relevant Technical Fields**

(i) UK Cl (Ed.M) C3V - UCD, UDB

(ii) Int Cl (Ed.5) C08B

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Search Examiner  
 M J PRICE

Date of completion of Search  
 23 DECEMBER 1993

Documents considered relevant  
 following a search in respect of  
 Claims :-  
 1-9

**Categories of documents**

- |   |   |
|---|---|
| <b>X:</b> Document indicating lack of novelty or of inventive step.   | <b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.        |
| <b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category. | <b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| <b>A:</b> Document indicating technological background and/or state of the art.   | <b>&amp;:</b> Member of the same patent family; corresponding document.   |

Category	Identity of document and relevant passages	Relevant to claim(s)
X	WPI Accession Number 87-219590/31 (CELLULOSE), & SU 1273793 (See abstract)	1 at least
X	WPI Accession Number 72-63319T/40 (HIGH MOLECULAR), & SU 325234 (See abstract)	1 at least

**PUB-NO:** GB002272447A  
**DOCUMENT-IDENTIFIER:** GB 2272447 A  
**TITLE:** Improvements in or relating  
to organic compounds  
**PUBN-DATE:** May 18, 1994

**INVENTOR-INFORMATION:**

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**APPL-NO:** GB09224101  
**APPL-DATE:** November 17, 1992

**PRIORITY-DATA:** GB09224101A (November 17, 1992)

**INT-CL (IPC):** C08B037/08

**EUR-CL (EPC):** C08B037/00 , C08L005/08 ,  
C08L097/00

**ABSTRACT:**

CHG DATE=19990617 STATUS=O> A polymeric product which is the reaction product of a) chitosan (herein defined as component A) with b) a

methoxyphenyl-containing aldehyde, ketone or acid (preferably in solution form) preferably derived from a natural product; the natural product preferably having a molecular weight of at least 10,000 and preferably being derived from lignin (herein defined as component B), e.g. veratraldehyde, salicylaldehyde, vanillin, syringaldehyde, etc. The product is film-forming and can be used in packaging.